TRIACYLGLYCEROL OLIGOMER PRODUCTS AND METHODS OF MAKING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001]   This application is a continuation of application No. 09/732,361, filed December 7, 2000, which is a non-provisional of U.S. provisional patent application Serial No. 60/169,468 filed December 7,1999, entitled "Vegetable Resin Products" and is hereby expressly incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED

RESEARCH OR DEVELOPMENT

[0002]   Not Applicable.

## BACKGROUND OF THE INVENTION

1.   Field of the Invention

[0003]   The present invention relates generally to triacylglycerol oligomer products and methods of making, using and producing same.

2.   Description of the Related Art

[0004]   Triacylglycerols(TAGS) are lipids of plant or animal origin. They include such common substances as safflower oil, canola oil, peanut oil, corn oil, cottonseed oil, sunflowerseed oil, linseed oil, soybean oil, tung oil, etc. Those TAGS that are liquids at room temperature are generally known as oils; those that are solids are usually known as fats. TAGS are simply the fatty acid esters of the triol glycerol. The general structure of TAGS is:

$$
\begin{array}{l}
CH2OCOR1 \\
| \\
R2COOCH \\
| \\
CH_2OCOR_3
\end{array}
$$
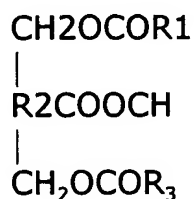
[0005]   The fatty acids, R1, R2, R3, that are obtained by hydrolysis of naturally occurring fats and oils are long, straight-chain carboxylic acids with about 12 to 20 carbon atoms. Most fatty acids contain even number of carbon atoms. Some of these common fatty acids are saturated, while others have one or more elements of unsaturation; generally carbon-carbon double bonds.

[0006]   TAGS naturally occur in some plants and can be obtained in relative pure forms by various processing methods. Substances such as free fatty acids and phospholipids are removed during processing. TAGS resulting from a single plant source after processing is a mixture made up of TAGS with differing percentages of saturated and unsaturated fatty acids.   Table 1 lists the

2

approximate composition of the fatty acids obtained from hydrolysis of some TAGS.

Table 1. Fatty Acid Composition Obtained by Hydrolyhsis of Common Triacylglycerols*

TAG	MYRISTIC	PALMITIC	STEARIC	OLEIC	LINOLEIC	ELEOSTEARIC	LINOLENIC
SOYBEAN	1 - 2	6 - 10	2 - 4	20 - 30	50 - 58		5 - 10
COTTON SEED	1 - 2	18 - 25	1 - 2	17 - 38	45 - 55		
CORN	1 - 2	7 - 11	3 - 4	25 - 35	50 - 60		
LINSEED		4 - 7	2 - 4	14 -30	14 - 25		45 - 60
SUNFLOWER		6 - 7	1 - 2	21 - 22	66 -67		
TUNG						80	

Table 2 list the supply of major TAGS produced in the United States.

TRIACYLGLYCEROL	PRODUCTION (POUNDS)
SOYBEAN	20,220,000,000
COTTONSEED	1,210,000,000
SUNFLOWERSEED	1,196,772,000
CORN	1,283,200,000

[0007] TAGS containing multiple double bonds within their carboxylic acid moieties will undergo thermal polymerization to form oligomers which are low molecular weight polymers. Triacylglycerol Oligomers(TAGOS) were first described by Schieber (1928).

[0008] Several investigators, Schieber(1928,1929), Kappelmier (1933,1938), Kurz(1936), Bradley (1940), Phalnikar and Bhide (1944), Bradley (1947), Barker, Crawford, and Hilditch(1951), Wisenblatt, Wells, and Common (1953), Wells and Common(1953), Pascual and Detera (1966), Boelhouwer, Knegiel, and Tels(1967), Saha and Bandyopadhyay (1974), Sarma (1984)) have suggested mechanisms for thermal polymerization of vegetable oils. Scheiber (1928,1929) and Kappelmeier (1933,1938) proposed a Diels-Alder diene synthesis as a basis for explaining the polymerization of vegetable oils which is often referred to in the literature. Most investigators agree with the formation of hydroxy unsaturated dimeric acids during thermal polymerization which are connected by means of a cyclic compound.

SUMMARY OF THE INVENTION

[0009]   In one embodiment, the present invention is a method for degumming triacylglycerols. This method includes the steps of: (A) providing a degummer assembly including a tank member haveing an inlet and an outlet, and an interior reaction chamber. The inlet and the outlet are in open fluid communication with the interior reaction chamber. Step B introduces a triacylglycerol mixture into the interior reaction chamber of the degummer assembly via the inlet. Step C introduces a liquid medium at a predetermined temperature into the triacylglycerol mixture in the interior reaction chamber of the tank member, thereby causing at least two reaction products to form. Step D separates at least two reaction products resulting from the triacylglycerol mixture and the liquid medium. Step E removes at least two reaction products from the interior reaction chamber of the tank member via the outlet in the tank member.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0010]   FIG. 1 is a perspective side view of the degummer assembly of the present invention.

[0011]   FIG. 2 is a second perspective side view of the degummer assembly of the present invention.

[0012]   FIG. 3 is a schematic flow diagram.

DETAILED DESCRIPTION OF THE INVENTION

[0013] Before explaining in detail at least one embodiment of the invention in detail by way of exemplary drawings, it is to be understood that the invention is not limited in its application to the details of construction and the arrangement of the components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for purpose of description and should not be regarded as limiting.

1.   Removal of Lecithin (Degumming)

[0014] Lecithin is a mixture of phospholipids, cephalin and inositol phosphatides, glycerides, traces of tocopherols and pigments. Phospholipids are lipids that contain groups derived from phosphoric acid. The most common phospholipids are the phosphoglycerides, which are closely related to common fats and oils. A phosphoglyceride generally has a phosphoric acid goup in place of one of the fatty acid groups of TAGS. The simplest class of lecithin are the phosphatidic acids, which consist of glycerol esterified by two fatty acids and one phosphoric acid group. Phosphatidic acid is represented by the chemical formula given below.

CH2OCOR1
|
CHOCOR2
|
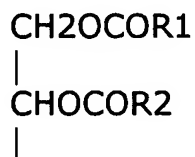
CH2OPO3H2

[0015]   Lecithin can be hydrated with water which renders it immiscible with oil and can brings about a separation of hydrated lecithin and oil. However, hydrated lecithin when mixed thoroughly with water and TAGS forms a very stable emulsion that separates only on standing for long periods of time. Formation of the emulsion can be avoided by bubbling TAGS through a container filled with water. A bubble chamber (degummer) was developed for this purpose.

[0016]   The degummer assembly 10 of the present invention is show in FIGS. 1 and 2. The degummer assembly 10 consists of a tank member 20 having an inlet 30, at least one outlet 40, and an interior reaction chamber 50. The inlet 30 and the at least one outlet 40 are in open fluid communication with the interior reaction chamber 50. A plate 60 containing small holes 70 of known diameter is placed at the bottom 80 of the tank member 20 and attached to inlet 30. The interior reaction chamber 50 is filled with a liquid medium 90 such as water or other liquids (bulk liquid) and maintained at a temperature which can range from <25°C to >60°C. Water hydrates the lecithin.

[0017]   TAG is pumped or gravity fed into the interior reaction chamber 50 through the small holes 70 and form bubbles 100 or "strings" on contact with the liquid medium 90 and do not form emulsions. The small bubbles 100 or

8

"strings" of TAGS rise to the surface of the bulk liquid and burst forming at least two separate liquid phases 110, (i.e. at least two reaction products) each of which remain separated from the liquid medium 90. At least one liquid phase contains degummed TAG 120, at least one liquid phase contains lecithin 130, and the third is the liquid medium 90.

[0018] As more and more TAG is fed into the tank member 20, the degummed TAG 120, which is less dense than the lecithin 130 rises to the top 140 of the interior reaction chamber 50 and forms a top layer 150. The lecithin 130 forms the middle layer. The lower layer is the liquid medium 90. The top layer 150 containing the degummed TAG 120 is allowed to reach a certain height to minimize contamination from the lecithin 130 at which time it can be continuously removed through the at least one outlet 40. The lecithin 130 can be removed through a lower at least one outlet tube 41. The volume produced depends on degummer assembly 10 variables such as the diameter of the small holes 70 of the inlet 30, size of the tank member 20, the flow rate, liquid medium 90 temperature, etc. Degummed TAG 120 was analyzed for phosphorous content. The results are given in Table 3 below.

Table 3.   Phosphorous Content of Degummed Triacylglycerols(TAGS)

[0019]TRIACYLGLYCEROL	[0020]PHOSPHOROUS, PPM*
[0021]SOYBEAN	[0022]0.005

[0023] Van Nieuwenhuyzen (1976) has demonstrated that the viscosity of lecithin at a temperature of 70°C increases as the moisture content decreases. The viscosity of the lecithin continues to increase until it achieves a moisture content of approximately 7%. The viscosity of the lecithin then begins to decrease rapidly until it is dry. This property of lecithin was used to develop a process to reduce the moisture content to less than 3%.

[0024] Lecithin can be separted according to the flow diagram shown in Figure 3. The lecithin 130 resulting from the degummer assembly 10 is passed into a separator or clarifier 160 to obtain a solids content of 15%. The concentrated lecithin mixture is then fed onto the porous cloth 170 of the conveyor system shown in Figure 3. The porous cloth 170 allows the water to pass through while retaining the net lecithin 130. The net lecithin 130 is then passed through a series of pressurized and heated rollers 180 which are in contact with each other. The first 190 and second 200 roller systems are made of stainless steel. The third 210 and fourth 220 roller systems are made of hard rubber. As the lecithin 130 passes through the series of pressurized and heated rollers 180 moisture is removed bringing about changes in viscosity resulting in the formation of a lecithin sheet 230 that contains less than 5% moisture on exiting from the series of pressurized and heated rollers 180. The moist lecithin sheet 230 is passed through an oven 240 heated with air and the moisture content of the lecithin sheet 230 is further reduced to less than 3%.

[0025] TAGS that have been degummed according to the procedure given above are further refined by vacuum distillation of free fatty acids. The first step in the process is to remove under vacuum a large portion of the oxygen before heat is applied. Once the oxygen is removed under vacuum heat is gradually applied until the boiling point temperature of free fatty acids have been reached at the operating vacuum. The temperature is maintained until all fatty acids have been removed. TAGS are now ready for thermal polymerization.

[0026] A continuous semi-plugged flow reactor has been designed for the refining of TAGS. All columns are under the same vacuum. Degummed TAG at room temperature is pumped into a first column and removal of oxygen begins. As TAG flows upward through column once the temperature increases to $60^{\circ}C$, it exits into column two. As it flows upward through column two oxygen is still being removed as the temperature gradually increases to $120^{\circ}C$. Columns three, four, and five are utilized for gradually increasing the TAG to the boiling point of free fatty acids at the operating vacuum and holding for a period of time depending on the flow rate to allow complete removal of the free fatty acids. At a temperature of 228°C - 235°C, TAG undergoes a color change from "straw" to a light greenish tint.

Table 4. Data for Refined Triacylglycerols

TRIACYLGLYCER L	Y*	R	B	FREE FATTY ACID - %*
SOYBEAN	[0027]2.8	[0028]1.4	[0029]92.0	
COTTONSEED				
SUNFLOWERSEED				
CORN				

[0030] TAGOS are prepared by thermal polymerization of TAGS that have been degummed and refined according to the procedures given above. Pre-polymerization and polymerization takes place in columns six through ten shown.

[0031] Column six is the pre-polymerization reactor column wherein the temperature is gradually increased from the boiling point of the free fatty acids to polymerization temperature. TAG exits column six and enters column seven at the polymerization temperature. Columns seven, eight, nine and ten are the reactor columns and are maintained at the polymerization temperature. TAG remains in the reactor columns for a residence time depending on the flow rate and exits into the storage tanks that are also under the same vacuum. The viscosity attained will depend on the residence time(flow rate) and the polymerization temperature.

Table 5. Viscosities of Triacylglycerol Oligomers for Various Residence Times and Temperatures.

TRIACYLGLYCEROL	RESIDENCE TIME	TEMPERATURE	VISCOSITY
SOYBEAN	24 hours	285C	32p
COTTONSEED	8 hrs	318C	154p
50% SUNFLOWERSEED + 50% SOYBEAN	13.5 hrs	295C	22p
CORN	13 hrs	295C	43p
50% SOYBEAN + 50% CANOLA	13 hrs	303C	11p
TUNG			

Table 8. Viscosity and Molecular Weight of Triacylglycerols Oligomers

[0032]TRIACYLGLYCEROL	VISCOSITY, CP	MOL. WEIGHT	MWD
SOYBEAN	12400	132785	57.5
SOYBEAN	3207	5569	3.7

[0033]   Skin color of face strongly depends on the type and amount of melanin and hemoglobin existing in the skin and varies widely according to several factors such as race, physiological conditions, age, sex, and seasonal variation. Face skin color is not uniform. It differs depending on whether it is the color of the forehead, forecheek, or sidecheek. Skin color was measured using photoelectric colorimeters and with the aid of computers, cosmetics were

13

formulated using TAGOS to exactly match skin colors. The formulation given below were used to prepare cosmetic colors.

Standard No. 1

Component	%
Cosmetic Brown-Lt	5.00
TAGOS Emulsion	95.00

Standard No. 2

Component	%
Raw Sienna	5.00
TAGOS Emulsion	95.00

Standard No. 3

Component	%
85% cosmetic Green + 15% Cosmetic Red	5.00
TAGOS Emulsion	95.00

[0034] An emulsion consisting of water and TAGOS was prepared using a lecithin sludge as the emulsifying agent. Lecithin sludge is the concentrated mixture of lecithin and water resulting from the degummer. TAGO, 62.7gms, and lecithin sludge (50-60%), 21.2gms, are mixed and heated to 70C. Water, 176.8gms, is heated in a separate container to 70C and then added to the TAGO and lecithin sludge mixture. The solution is stirred and allowed to cool. The pigment is added and the mixture is homogenized.

[0035] A Lovibond Tintometer was used to measure skin color. The instrument was standardized according to procedure using a gray scale and magnesium oxide standard. Measurements were made on the right cheek, left

14

cheek, and the forehead. The skin color of 234 females was measured using the Lovibond Tintometer. This data is given in Table 12.

[0036] A thin layer of cosmetic preparation was placed on a filter paper and allowed to dry. The probe from the Lovibond Tintometer is placed directly on the dry cosmetic color preparation and the color determined and recorded. This data is given in Table 11.

[0037] A computer program was written for a Radio Shack Tridos 80 Computer to perform the calculations. Color matching functions of Banks (1977) were used to write the computer program. The program is written in four parts and is given in Table 10. The program produces tristimulus values, ratio of the standard cosmetic preparation to match the the skin color, and the difference between the skin color and the calculated color match formulation. These results are given in Table 12.

Table 10. Computer Program for Color Matching - Four Parts

Part 1 ' FORMULA'

```
1 DIM TR(39), TY(39), TB(39), E(39), EY(39), EZ(39)
10 REM CALCULTAION OF CHROMATICITY COORDINATRES AND TRISTIMULUS
VALUES CALL TRISTIM
20 REM READ LOVIBOND SPECTRAL INTERNAL TRANSMITTANCES
40 FOR I = 0 TO 39
50 READ TR(I), TY(I), TB(I)
60 NEXT
70 REM READ CIE 1931 COLOR-MATCHING FUNCTIONS WEIGHTED BY
RELATIVE SPECTRAL POWER DISTRIBUTIONS OF CIE STANDARDS
80 FOR I = 0 TO 39
90 READ EX(I), EY(I), EZ(I)
100 NEXT
130 DATA .90258, .02889, .99815
131 DATA .90352, .12593, .99809
132 DATA .90439, .25435, .99788
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(10)

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133 DATA .90603, .39957, .99711
134 DATA .90737, .52037, .99573
135 DATA .90824, .61634, .99363
136 DATA .90886, .70289, .99111
137 DATA .90858, .77822, .98800
138 DATA .90722, .84481, .98338
139 DATA .90444, .89471, .97459
140 DATA .89819, .92976, .96004
141 DATA .88633, .95277, .94109
142 DATA .86526, .96755, .92316
143 DATA .83257, .97738, .89900
144 DATA .79598, .98364, .87326
145 DATA .77392, .98754, .84574
146 DATA .78952, .99040, .83553
147 DATA .83317, .99195, .85049
148 DATA .87817, .99236, .86792
149 DATA .91300, .99247, .85702
150 DATA .93628, .99179, .81808
151 DATA .95268, .99073, .77002
152 DATA .96362, .98933, .76498
153 DATA .97109, .98768, .77420
154 DATA .97648, .98599, .77827
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155 DATA .98053, .98438, .77386
156 DATA .98348, .98333, .76119
157 DATA .98572, .98287, .76656
158 DATA .98753, .98279, .78191
159 DATA .98892, .98330, .83172
160 DATA .99012, .98405, .88572
161 DATA .99117, .98449, .93507
162 DATA .99194, .98510, .96744
163 DATA .99247, .98627, .98466
164 DATA .99303, .98789, .99228
165 DATA .99336, .98912, .99587
166 DATA .99365, .99014, .99719
167 DATA .99402, .99108, .99770
168 DATA .99420, .99160, .99790
169 DATA .99430, .99210, .99800
180 DATA .004,  .000,  .020
181 DATA .019,  .000,  .089
182 DATA .085,  .002,  .404
183 DATA .329,  .009, 1.57
184 DATA 1.238,  .037,  5.949
185 DATA 2.997,  .122,  14.628
186 DATA 3.975,  .262,  19.938
187 DATA 3.915,  .443,  20.638
188 DATA 3.362,  .694,  19.299
189 DATA 2.272, 1.058,  14.972
190 DATA 1.112, 1.618,  9.461
191 DATA .363,  2.358,  5.274
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(11)

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192 DATA .052,  .3.401,  2.864
193 DATA .089,  4.833,  1.520
194 DATA .576,  6.462,  .712
195 DATA 1.523, 7.934,  .388
197 DATA 4.282, 9.832,  .086
198 DATA 5.880, 9.841,  .039
199 DATA 7.322, 9.147,  .020
200 DATA 8.417, 7.992,  .016
201 DATA 8.984, 6.627,  .010
202 DATA 8.949, 5.316,  .007
203 DATA 8.325, 4.176,  .002
204 DATA 7.070, 3.153,  .002
205 DATA 5.309, 2.190,  .000
206 DATA 3.693, 1.443,  .000
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207 DATA 2.349,  .886,  .000
208 DATA 1.361,  .504,  .000
209 DATA  .708,  .259,  .000
210 DATA  .369,  .134,  .000
211 DATA  .171,  .062,  .000
212 DATA  .082,  .029,  .000
213 DATA  .039,  .014,  .000
214 DATA  .019,  .006,  .000
215 DATA  .008,  .003,  .000
216 DATA  .004,  .002,  .000
217 DATA  .002,  .001,  .000
218 DATA  .001,  .001,  .000
219 DATA  .001,  .000,  .000
300 REM CALCULATIONS OF TRISTIMULUS VALUES
310 U = 0
320 V = 0
330 W = 0
340 PRINT "INPUT Y" : INPUT Y
350 PRINT "INPUT R" : INPUT R
360 PRINT "INPUT B" : INPUT B
370 FOR I = 0 TO 39
380 RYB = ((TR(I))[R)*((TY(I)[Y))*((TB(I)[B))
390 U = U + ( RYB * EX(I))
400 V = V + ( RYB + EY(I))
410 W = W + ( RYB + EZ(I))
420 NEXT
430 UVW = U + V + W
440 UBAR = U/UVW
450 VBAR = V/UVW
460 WBAR = W/UVW
470 X =U: LPRINT " X = ";X
480 Y1 = V: LPRINT "Y = ";Y1
490 Z  = W: LPRINT "Z = ";Z
500 OPEN "O",1, "VALUES"
510 PRINT#1,X;Y1;Z
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(12)

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520 CLOSE 1
530 OPEN"O",1,"LOVIBOND"
540 PRINT#1,Y;R;B
550 CLOSE 1
560 RUN "FORMULA1"
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Part 2 'FORMULA1'

```
10 DIM TR(15), TY(15), TB(15), ME(16,3), T(16,3), Y(3), R(3), B(3), F(1),
D(16,16)
40 FOR I = 0 TO 15
50 READ TR(I), TY(I), TB(I)
60 NEXT
132 DATA .90439, .25435, .99788
134 DATA .90737, .52037, .99573
136 DATA .90886, .70289, .99111
138 DATA .90722, .84481, .98338
140 DATA .89819, .92976, .96004
142 DATA .86526, .96755, .92316
144 DATA .79598, .98364, .87326
146 DATA .78952, .99040, .83553
148 DATA .87817, .99236, .86792
150 DATA .93628, .99179, .81808
152 DATA .96362, .98933, .76498
154 DATA .97648, .98599, .77827
156 DATA .98348, .98333, .76119
158 DATA .98753, .98279, .78191
160 DATA .99012, .98405, .88572
162 DATA .99194, .98510, .96744
330 FOR I = 1 TO 3
350 READ Y(I), R(I), B(I)
355 LPRINT "    ":LPRINT Y(I), R(I), B(I)
360 NEXT
365 LPRINT " ":LPRINT "T1", "T2", "T3"
367 OPEN"O",1,"DYES"
370 J = 0
380 FOR I = 0 TO 15
385 J = J + 1
390 FOR N = 1 TO 3
410 Q = (TR(I)[R(N))*(TY(I)[Y(N))*(TB(I)[(N))
420 T(J,N) = (1-Q)[2/(2*Q)
430 NEXT
440 PRINT#1, T(J,1); T(J,2); T(J,3)
445 LPRINT "    " : LPRINT T(J,1), T(J,2) T(J,3)
450 NEXT
460 CLOSE 1
465 GOTO 600
470 J = 0
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480 OPEN "O",1,"SAMPLE"
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505 LPRINT " ": LPRINT  "F", "D"
510 FOR I = 0 TO 15
520 J = J + 1
530 Q = (TR(I)[X2)*(TY(I)[X1)*(TB(I)[X3)
540 F(J) = (1-Q)[2/(2*Q)
550 D(J,J) = -((4*Q)*(1-Q)+((1-Q)[2)*2)/(4*(Q[2))
560 PRINT#1, F(J);D(J,J)
565 LPRINT "   ":LPRINT F(J), D(J,J)
570 NEXT
580 CLOSE 1
590 RUN "FORMULA2"
600 OPEN"I",1,"LOVIBOND"
610 INPUT#1,X1,X2,X3
620 CLOSE 1
630 GOTO 470
700 DATA 1.9, 3.7, 0
710 DATA 3.6, 4.0, 0
720 DATA 1.4, 1.2, 0
```

Part 3 "FORMULA2"

```
100 DIM ME(16,3), D(16,16), B(3,16), M(3,16), F(16,1), R(3,3), A(3,3),
V(3,1),T(16,3), C(3,1)
105 LPRINT "   ": LPRINT "EX-BAR, "EY-BAR", "EZ-BAR"
110 OPEN"I",1, "FUNCTION"
120 FOR I = 1 TO 16
140 INPUT#1, M(1,I), M(2,I), M(3,I)
170 NEXT
180 CLOSE 1
190 OPEN "1",1,"SAMPLE"
200 FOR I = 1 TO 16
210 INPUT#1, F(I,1), D(I,1)
215 D(I,1), = 1/D(I,1)
220 NEXT
230 CLOSE 1
240 FOR 1 = 1 TO 3
250 FOR J = 1 TO 16
260 B(I,J) = 0
270 FOR K = 1 TO 16
280 B(I,J) = B(I,J) + M(I,K)*D(K,J)
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290 NEXT K
300 NEXT J
310 NEXT I
315 FOR J = 1 TO 16
316 LPRINT "   ":LPRINT B(1,J),B(2,J),B(3,J)
317 NEXT
320 OPEN "I",1,"DYES"
330 FOR I = 1 TO 16
340 INPUT#1, T(I,1), T(I,2), T(I,3)
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```
350 NEXT
360 CLOSE 1
370 FOR I = 1 TO 3
380 FOR J = 1 TO 3
390 R(I,J) = 0
400 FOR K = 1 TO 16
410 R(I,J) = R(I,J) + B(I,K)*T(K,J)
420 NEXT K
430 NEXT J
440 NEXT I
445 GOSUB 1000
450 GOSUB 18000
460 FOR I = 1 TO 3
470 C(I,1) = 0
480 FOR K = 1 TO 16
490 C(I,1) = C(I,1) + B(I,K)*F(K,1)
500 NEXT K
510 NEXT I
520 FOR I = 1 TO 3
530 V(I,1) = 0
540 FOR K = 1 TO 3
550 V(I,1) = V(I,1) + A(I,K)*C(K,1)
560 NEXT K
570 NEXT I
580 LPRINT " C1 EQUALS " ; V(1,1): LPRINT "   "
590 LPRINT " C2 EQUALS " ; V(2,1): LPRINT "   "
600 LPRINT " C3 EQUALS " ; V(3,1): LPRINT "   "
610 OPEN "O",1, "INVERSE"
620 FOR I = 1 TO 3
630 PRINT#1, A(I,1);A(I,2);A(I,3)
640 NEXT
650 CLOSE 1
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660 OPEN "O",1, "CONCN"
670 PRINT#1, V(1,1); V(2,1); V(3,1)
680 CLOSE 1
690 RUN "FORMULA3"
1000 PRINT "THE MATRIX TO BE INVERTED IS: ": PRINT
1010 FOR I = 1 TO 3: FOR J = 1 TO 3 : LPRINT R(I,J): NEXT J: PRINT :
NEXT I
1020 RETURN
18000 CLS: REM SUBROUTINE TO INVERT AN N X N MATRIX. A(N,N) IS THE
INPUT
18001 GOTO 18009: INPUT "DO YOU WANT DOUBLE PRECISION";A$
18002 IF LEFT$(A$,1) = "N" THEN 18009
18004 DEFDBL A-H, O-Z
18009 DEFINT I,J,N
18010 N = 3
18050 FOR I = 1 TO N: A(I,1) = 1: NEXT
18052 CLS: PRINT " YOUR MATRIX IS: ":PRINT
                              (15)
18054 FOR I = 1 TO N: FOR J = 1 TO N: I3!=R(I,J):PRINT I3!;
:NEXT:PRINT :NEXT
18060 I1 = I1 + 1: IF  I1 = N + 1 THEN 18210: REM WE'RE THROUGH!
18070 IF  R(I1,I1) = 0  THEN GOSUB 18130 : REM INTERCHANGE ROWS
18080 REM NORMALIZE DIAGONAL ELEMENT AND ZERO COLUMN IN OTHER
ROWS.
18090 Q = R(I1,I1): FOR J = I1 TO N: R(I1,J) = R(I1,J)/Q: NEXT
18095 FOR J = 1 TO N: A(I1,J) = A(I1,J)/Q: NEXT
18100 FOR I = 1 TO N: IF I = I1 THEN 18117
18105 Q = R(I,I1)
18110 FOR J = I1 TO N: R(I,J) = R(I,J) - Q*R(I1,J): NEXT
18115 FOR J = 1 TO N: A(I,J)=A(I,J)-Q*A(I1,J): NEXT
18117 NEXT I
18120 GOTO 18060
18130 REM INTERCHANGE ROWS TO PREVENT ZERO DIVIDE
18140 I2 = I1: IF I2 = N THEN 18170
18150 I2 = I2 = I2 + 1: IF I2 = N THEN 18170
18160 IF R(I2,I1) = 0  AND I2<N THEN 18150
18170 IF I2 = N THEN PRINT " DETERMINENT = 0 ! ! ! ": STOP
18180 FOR I = I1 TO N
18190 T = R(I1,I):R(I1,I) = R(I2,I): R(I2,I) = T
18200 S = A(I1,I):A(I1,I) = A(I2,I):A(I2,I) = S:NEXT: RETURN
18210 GOSUB 18230; FOR I = 1 TO N: FOR J = 1 TO N: PRINT A(I,J): NEXT
J: PRINT:
```

```
18220 RETURN
18230 PRINT " THE INVERSE OF YOUR MATRIX IS : ": PRINT:RETURN
19000 REM INPUT ELEMENTS BY ROW
19010 PRINT "ENTER THE ELEMENTS ONE AT A TIME BY ROW AND PRESS
ENTER"
19020 FOR I = 1 TO N: FOR J = 1 TO N
19030 INPUT R(I,J): NEXT J,I
19040 GOTO 18050
```

Part 4 'FORMULA3'

```
100 DIM FM(16,1), TM(3,1), T(16,3), V(3,1) M(3,16), RM(16,1)
110 OPEN "I",1, "DYES"
120 FO;R i = 1 TO 16
130 INPUT#1, T(I,1), T(I,2), T(I,3)
140 NEXT
150 CLOSE 1
160 OPEN "I",1, "CONCN"
170 INPUT#1, V(1,1), V(2,1), V(3,1)
180 CLOSE 1
190 FOR I = 1 TO 16
200 FM(I,1) = 0
210 J = 1 TO 3
220 FM(I,1) = FM(I,1) + T(I,J) + V(J,I)
```

(16)

```
230 NEXT J
240 NEXT I
250 GOTO 500
260 OPEN "I",1, "FUNCTION"
270 FOR I = 1 TO 16
280 INPUT#1, M(1,I), M(2,I), M(3,I)
290 NEXT
300 CLOSE 1
310 FOR I = 1 TO 3
320 TM(I,1) = 0
330 FOR K = 1 TO 16
340 TM(I,1) = TM(I,1) + M(I,K)*RM(K,I)
350 NEXT K
360 NEXT I
370 OPEN " O",1, "TRISTIM"
380 PRINT#1, TM(1,1);TM(2,1);TM(3,1)
```

23

```
390 CLOSE 1
400 LPRINT "   " : LPRINT "   "
410 LPRINT "TRISTIMULUS VALUES FOR MATCH": LPRINT "    "
420 LPRINT " X = "; TM(1,1):LPRINT "    "
430 LPRINT " Y = "; TM(2,1):LPRINT "    "
440 LPRINT " Y=" "; TM(3,1):LPRINT "    "
450 RUN "FORMULA4"
500 FOR I = 1 TO 16
510 B1 = 2*(1+FM(I,1))
520 B2 = B1[2
530 RM(I,1) = (B1 - SQR(B2-4))/2
540 NEXT
550 GOTO 260
```

Part 5 "FORMULA4"

```
6000 REM CALCULATIONS OF COLOR DIFFERENCE
6005 DIM DT(3,1), TM(3,1), A(3,3), DC(3,1), V(3,1), VXS(1), VYS(1), VZS(1)
6010 PRINT "INPUT VX, VY, VZ FOR SAMPLE"
6020 INPUT VXS(1), VYS(1), VZS(1)
6060 PRINT "INPUT VX, VY, VZ FOR MATCH"
6065 INPUT MXV: INPUT MYV: INPUT MZV
6067 FOR I = 1 TO 1
6210 DVY = ((0.23)*(VYS(I) - MYV))[2
6215 D1VXY = (( VXS(I) - VYS(I)) - (MXV -MYV))[2
6220 D2VZYY = (VZS(I) -VYS(I)) - (MZV - MYV)
6225 D3VZY = ((0.4)*(D2VZYY))[2
6230 DE = (DVY + D1VXY + D3VZY)[(1/2)
6235 DE = 40*DE
6237 NEXT
```

```
6238 LPRINT "   "; LPRINT "   "
62440 LPRINT "  THE VALUE FOR THE COLOR DIFFERENCE IS  "; DE; LPRINT "  "
6250 PRINT " TO CONTINUE ITERATION , 'ENTER' 1. ": PRINT "   "
6260 PRINT " TO DISCONTINUE ITERATION, 'ENTER' 2. ": PRINT "    "
6270 INPUT ZZ
6280 ON ZZ GOTO 10000, 6300
6300 END
```

```
10000 OPEN "I", 1,1 "VALUES"
10010 INPUT#1, X, Y, Z
10020 CLOSE 1
10030 OPEN "I",1, "TRISTIM"
10040 INPUT#1, TM(1,1), TM(2,1), TM(3,1)
10050 CLOSE 1
10060 DT(1,1) = X - TM(1,1)
10070 DT(2,1) = Y - TM(2,1)
10080 DT(3,1) = Z - TM(3,1)
10090 OPEN "I" ,1, "INVERSE
10100 FOR I = 1 TO 3
10110 INPUT#1, A(I1,). A(I2,), A(I3)
10120 NEXT
10130 CLOSE 1
10140 FOR I = 1 TO 3
10150 DC(I,1) = 0
10160 FOR K = 1 TO 3
10170 DC(I,1) = DC(I,1) + A(I,K)*DT(K,I)
10180 NEXT K
10190 NEXT I
10200 OPEN "I",1, "CONCN"
10210 INPUT#1, V(1,1), V(2,1), V(3,1)
10220 CLOSE 1
10230 V(1,1) = V(1,1) + DC(1,1)
10240 V(2,1) = V(2,1) + DC(2,1)
10250 V(3,1) = V(3,1) + DC(3,1)
10260 LPRINT "   "; LPRINT "   "
10270 LPRINT " C1 =   ";V(1,1) : LPRINT "   "
10280 LPRINT " C2 =   ";V(2,1) : LPRINT "   "
10290 LPRINT " C3 =   ";V(3,1) : LPRINT "   "
10300 OPEN "O",1, "CONCN"
10310 PRINT#1, V(1,1), V(2,1), V(3,1)
10320 CLOSE 1
10330 RUN "FORMULA3"
10340 END
```

Table 11. Color of Standard Soybean Cosmetic Formulations -

NUMBER	Y	R	B
1	1.9	3.7	0
2	3.6	4	0
3	1.3	1.2	0

Table 12. Skin Color of Females-

NUM	COLOR	RANGE	HUE	VALUE	CHR	X-BAR	Y-BAR	Z-BAR	Y	DE
12	1	1	7.53 YR	4.86	4.03	0.4034	0.3733	0.2234	19	1-4
29	2	2	6.79 YR	4.43	3.54	0.4	0.3619	0.2388	15	4-7
13	3	2	6.63 YR	6	3.5	0.3761	0.3563	0.2677	30	11-12
12	4	4	5.29 YR	3.59	2.99	0.3964	0.356	0.2546	10	7-9
15	5	4	5YR	5.34	3.75	0.3848	0.3562	0.259	23	9-10
22	6	5	4.27 YR	4.68	3.01	0.3777	0.3509	0.2717	17	12-13
5	7	6	3.06 YR	5.73	4.62	0.3968	0.3528	0.2504	27	10-11
10	8	6	3.26 YR	4	2.19	0.3668	0.3403	0.2929	12	17-18
44	9	7	2.5YR	4	2.86	0.3832	0.344	0.2727	12	14-15
36	10	7	2.47 YR	4.68	3.36	0.3818	0.3464	0.2718	17	13-14
19	11	8	10R	4.68	3.71	0.388	0.3417	0.2708	17	15-16
17	12	8	10R	6	5.38	0.3633	0.3478	0.2889	30	16-17

Preparation of Triacylglycerol Oligomers Cosmetics

1. Cold Cream

Soybean Z- 6	40.1%
Lecithin Sludge	8.1%
Water	51.8%

2. Lotion

Soybean Z - 3	30.1%
Lecithin Sludge	8.1
Water	60.8%

3. Foundation

Soybean Z - 8	25.0%
Lecithin Sludge	8.0%
Water	57.0%
Pigment	10.0%

4. Lipstick

Soybean Z - 10	40.0%
Lecithin	8.0%
Water	42.0%
Pigment	10.0%

5. Pucker Paint

Soybean Z - 5	37.3%
Lecithin Sludge	8.0%
Water	44.7%
Pigment	10.0%

6. Blusher

Soybean Z - 6	37.9%
Lecithin Sludge	8.0%
Water	44.1%
Pigment	10.0%

7. Mascara

Soybean Z - 9	48.0%
Lecithin Sludge	8.0%
Water	34.0%
Carbon Black	10.0%

[0038]   Color has three qualities which are hue, value and chroma or intensity. Hue is the quality which distinguishes one color from another, for example red or blue. It is the name of the color family. The lightness or darkness of a color is called value. We can visualize how light or how dark a color is by comparing it with a value scale showing black at the bottom and white at the top. The third dimension of color is chroma or intensity. It is often thought of as the strength or weakness of a color. We can think of intensity as the degree to which a color departs from a neutral gray of the same value.

[0039]   A pleasing combination of colors is known as a color harmony. One of the greatest teachers of color harmony is nature. This phenomenon is apparent in everything that grows. Nature presents a protusion of colors, beautifully arranged and spaced is as to present a pleasing spectacle to the eye. Flowers of strong and weak colors are striking against their background. Trees in the fall of the year are never more harmonious than in their bright color

schemes of red, orange, yellow, and purple against the background of clear blue sky with fading green grass and brown earth in the foreground. These colors brings a change of hues, values, and chroma, and presents a beautiful color scheme. There are four general ways to combine colors; contrast in hue, value, chroma and area. The Munsell color theory suggests three paths for color harmony: The first path is vertical with rapid changing value. We refer to this color harmony as SOPHISTICATED. The second path is lateral. This is a rapid change of hues adjacent on the color wheel. We refer to this color harmony as EXOTIC. The third path is inward. The inward path leads to the neutral center and onto the opposite on the Munsell color wheel. We refer to this color harmony as PROVACATIVE.

[0040] Using the color of the skin, the color of the eyes, the color of the hair and a related red a computer program was developed to produce sophisticated, exotic, and provocative color harmony schemes for skin colors shown in Table 13.

Table 13. Listing for Cosmetic Wardrobe Computer Program

Table 14. Color Harmony Data for Color No. 35

C LOR	HUE	VALUE	CHR MA
HAIR	4.5R	2.3	4.5
EYES	6.7B	3.4	1.2
SKIN	3.5yr	4.4	3.3
RELATED RED	4.4r	2.3	1.4

Table 15. Color Harmony Data for Color No. 45

COLOR	HUE	VALUE	CHROMA
HAIR	4.5	4.5	4.5
EYES	6.7	6.7	6.7
SKIN	8.9	8.9	8.9
RELATED RED	6.7	6.7	6.7

Table 16. Cosmetic Wardrobe Listing for Color No.35

COSMETIC	CODE
COLOR DIFFERENCE	1.98
FOUNDATION ·	DEEP COCOA #11
BLUSHER	TITIAN
LIPSTICK	#11
DAZZLE DUST	VIOLET
PUCKER PAINT	CURRANT

Table 17. Cosmetic Wardrobe for Color No. 45

COSMETIC	CODE
COLOR DIFFERENCE	0.456
FOUNDATION	DEEP COCOA #11
BLUSHER	BURGUNDY
LIQUID LINER	BROWN
MASCARA	BLACK
LIPSTICK	4
LIPGLOSS	4
DAZZLE DUST	BRONZE FROST
PUCKER PAIN	AMETHYST

[0041] Heat-set web offset ink was introduced in the 1950's as a printing process and is used for the production of magazines, catalogues and brochures. All heat-set inks are expected to fulfill exacting criteria, in addition to properties of cold-set ink, such as high gloss and dry quickly in an oven. Heat-set ink are dried by passing the printed web of paper through an oven using high velocity hot air; sufficient to raise the temperature of the to 100-140C. TAGOS ink has been formulated which meet the criteria of heat-set web offset ink and does not need to be passed through an oven for drying. This is accomplished by formulating printing ink using TAGOS of viscosity above 300 poises to obtain high gloss and rub-off resistance. Quick drying is accomplished by using a drying agent.

Table 18. Soybean Oligomer Printing Ink - Formula I

SUBSTANCE	PERCENT
CARBON BLACK	20
SOYBEAN OLIGOMER Z - 6	71
CLAYTONE HY	9

Table 19. Soybean Oligomer Printing Ink - Formula II

SUBSTANCE	PERCENT
CARBON BLACK	20
SOYBEAN OLIGOMER Z - 6	70
CLAYTONE HY	9
COBALT ACETATE	1

Table 20. Soybean Oligomer Printing Ink - Formula III

SUBSTANCE	PERCENT
CARBON BLACK	15
SOYBEAN OLIGOMER Z - 10	30
SOYBEAN OLIGOMER Z - 3	40
CLAYTONE HY	9
COBALT ACETATE	1

Table 21. Soybean Oligomer Printing Ink - Formula IV

SUBSTANCE	PERCENT
CARBON BLACK	20
SOYBEAN OLIGOMER Z - 6	61
CLAYTONE HY	9
POLYOL	10

Table 22. Cottonseed Oligomer Printing Ink - Formula V

SUBSTANCE	PERCENT
CARBON BLACK	20
COTTONSEED OLIGOMER	71
CLAYTONE HY	9
COBALT ACETATE	1

Table 23. Sunflowerseed Oligomer Printing Ink - VI

SUBSTANCE	PERCENT
CARBON BLACK	20
SUNFLOWERSEED OLIGOMER	71
CLAYTONE HY	9
COBALT ACETATE	1

Table 24. Corn Oligomer Printing Ink - VII

SUBSTANCE	PERCENT
CARBON BLACK	20
CORN OLIGOMER	71
CLAYTONE HY	9
COBALT ACETATE	1

Table 25. N,N'-di-n-butyl-N$_a$-lauroyl Glutamide(BLG) Soybean Oligomer Printing Ink - VIII

SUBSTANCE	PERCENT
CARBON BLACK	20
BLG-SOYBEAN OLIGOMER*	71
CLAYTONE - HY	9

* Preparation given in Section VI

Table 26. Thermosetting Epoxy Printing Ink

SUBSTANCE	PERCENT
EPOXY(I) SOYBEAN*	70
PHTHALO BLUE PIGMENT	15
SOLVENT	5
HyTONE	5

* See Section IX

Table 27 Fountain Solution

SUBSTANCE	PERCENT
A B DICK UNIVERSAL	95
T-BUTYL HYDROPEROXIDE	5

[0042]   In screen printing the ink is forced through the open areas of a stencil supported on a mesh of synthetic fabric stretched across a frame. The ink is mechanically forced through the mesh onto the substrate underneath by drawing a squeegee across the stencil. These inks are high viscosity, low tack, short cure times, and good color retention after several wash cycles. TAGOS were formulated to meet these criteria.

Table. 30. Screen Printing Ink - Formula I

SUBSTANCE	PERCENTAGE
CI PIGMENT RED 49	20
SUNFLOWERSEED OLIGOMER	30
SOYBEAN OLIGOMER Z - 6	50

Table 31. Screen Printing Ink - Formula II

SUBSTANCE	PERCENTAGE
CI PIGMENT RED 49	20
SUNFLOWERSEED OLIGOMER	30
SOYBEAN OLIGOMER X - Y	50

Table 32. Screen Printing Ink - Formula III

SUBSTANCE	PERCENT
CI PIGMENT RED 49	20
SUNFLOWERSEED OLIGOMER Z-6	30
SOYBEAN OLIGOMER Z-6	25
SOYBEAN OLIGOMER X - Y	25

Table 33. Screen Printing Ink - Formula IV

SUBSTANCE	PERCENT
BLUE DYE	10
SOYBEAN OLIGOMER Z - 6	25
WATER	74.98
THICKNER	0.1
COBALT ACETATE	0.1

Table 34. Screen Printing Ink - Formula V

SUBSTANCE	PERCENT
BLUE DYE	10
COTTONSEED OLIGOMER	25
WATER	74.98
THICKNER	0.1
COBALT ACETATE	0.1

Table 35. Screen Printing Ink - Formula VI

SUBSTANCE	PERCENT
BLUE DYE	10
SUNFLOWERSEED OLIGOMER	25
WATER	74.98
THICKNER	0.1
COBALT ACETATE	0.1

Table 36. Screen Printing Ink - Formula VII

SUBSTANCE	PERCENT
BLUE DYE	10
CORN OLIGOMER	25
WATER	74.98
THICKNER	0.1
CORN	0.1

[0043]   The inks were printed on cotton and coated cotton fabrics and allowed to dry. The printed fabrics were then washed and dried. The color was measured before and after each wash cycle to determine color fastness.

Table 37. Color Fastness of Screen Printed Uncoated Cotton Fabrics

INK FORMULA	L*	a*	b*	L*	a*	b*	Gray Change-	Difference
I	36.31	43.35	12.60	37.59	38.00	9.97	3.00	6.10
II								
III								
IV	38.99	-14.21	-39.57	40.96	12.85	35.00	3.00	5.16
V								
VI								
VII								

Table 38. Color Fastness of Screen Printed Coated Cotton Fabrics

INK FORMULA	COLOR BEFORE			COLOR AFTER			Gray Change- Difference	
	L*	a*	b*	L*	a*	b*		
I	37.63	47.09	12.42	39.55	44.52	9.44	3.00	4.37
II								
III								
IV	38.99	-14.21	-39.57	40.96	-12.85	35.00	- 3.00	5.16
I								

[0044] Although many valuable products are fabricated each day from fibers, these items could never exist unless a finish had been applied to the fibers during the extrusion or spinning process. Fabric finishing is intended to provide a special performance characteristics or properties to a textile fabric. This can be the development of dimensional control or resistance to wrinkling during use. The characteristics may be the provision of permanent crease and smooth drying performance or the requirement for the fabric to withstand subsequent processing steps. There may be the need for a finish to impart resistance to end use exposure, i.e., water or oil repellency or resistance to crocking or bleeding. Of equal importance is the need to provide the finished fabric with improved or changed aesthetic properties. TAGOS were developed for applications in sizing and finishing.

[0045] Solutions to size fabrics were made according to the formula given in Table 39. TAGOS were soybean, cottonseed, sunflowerseed, and corn. Strips of gauzy cotton fabric (5 x 30 cm were padded twice at 25C to ca. 110% wet pick-up, followed by drying at 120C for 3 minutes and conditioning for 48 hours at 65% relative humidity and at room temperature.

[0046] Textile finishers were made using soybean, cottonseed, sunflowerseed, and corn oligomers according to the formula given in Table 40. Poplin cotton fabric pieces (30 x 45 cm) were padded twice at room temperature in the finish solution to ca. 80% wet pick-up, followed by drying

(100C/3 min.) and curing (160C/3 min.). The cured samples were then given an after wash in a bath containing 1g/l sodium carbonate along with 1g/l on triton X-100 at 55C for 15 minutes./ rinsed, and air dried, and conditioned.

Table 39. Formula for Textile Sizers

SUBSTANCE	PERCENTAGE
TAGO	12
TRITON X - 100	5
WATER	83

Table 40. Formula for Textile Finishers

SUBSTANCE	PERCENTAGE
TAGO	25
WATER	65
MAGNESIUM CHLORIDE HEXAHYDRATE	5
TRITON X-100	5

[0047]   Historically, reactions on polymers have been of major importance, as they have made possible the applications of cellulose as textile fibers, plastics, coatings, and even explosives. Reactions of polymers can occur with oxygen, irradiation, heat, moisture, and bacterial attack which induces the problem of "aging" of polymeric materials. The most important of them are atmospheric oxygen and irradiation, since they are most likely to induce chain scission. Polymers can undergo chemical reactions by chemical modification of

40

the functional groups of the polymers. As discussed earlier a Diels-Alder diene synthesis was used as a basis for explaining the polymerization of TAGOS which is most often referred to in the literature. Most investigators agree with the formation and presence of hydroxyl groups, carboxylic acid groups, cyclic compounds, and double bonds during thermal polymerization. These functional groups along with the ester group provide the basis for producing polymers from TAGOS.

[0048] An equivalency based on hydroxyl number of the glycol and assumed hydroxyl number of TAGOS per molecule was calculated. The hydroxyl number for glycol was two and the hydroxyl number for TAGO varied for each experiment. The equivalency mass for glycol was the molecular weight divided by two. The equivalency mass for TAGOS was obtained by dividing the apparent molecular weight by the hydroxyl number for each experiment. Apparent molecular weights were determined by gel permeation chromatography. An illustrative example was the formation of complexes between soybean oligomer (SBO) and ethylene and propylene glycol. The apparent molecular weight of SBO was 10,000.

[0049] A series of experiments were conducted using N,N' - di n-butyl-N_a-lauroyl glutamide (BLG) to crosslink TAGOS. One gram of BLG was dissolved in 99grams of TAGOS and heated to 150°C. The solution viscosity increased depending on the amount of BLG added.

41

Table 43.   Triacylglycerol Oligomer   Complexes with Ethylene and Propylene Glycol

TAGOS	VISCOSITY	HYDROXYL*	MOL. WT.	GLYCOL	RATIO	VISCOSITY
SOYBEAN	22683cp	10	10000	ETHYLENE	1::1	17733cp
SOYBEAN	22683cp	10	140000	PROPYLENE	1:01	17983cp

[0050]   When ethylene glycol, 10 grams, was mixed with SBO, 300 grams, the solution thickened and became very turbid. The mixture was heated up to a temperatures of 120°C and a white vapor was given off. The mixture was removed from the hot plate for thirty minutes after which time the mixture was replaced on the hot plate and heating continued.   No vapors were given off after heating for 3.75 hours. After heating for more than six hours the mixture became completely clear with the appearance of small crystal like substances at the bottom if the flask. After more than nine hours of heating, the mixture was removed from the heat and allowed to cool.   As it cooled down to room temperature it became a turbid viscous mixture.

[0051]   SBO, 306 grams, was mixed with propylene glycol, 10 grams, in an Erlenmeyer flask. The mixture remained clear after mixing. The mixture was heated to a temperature of 120° C. The mixture was heated to a temperature of 115° at which time white vapors were given off. However, the mixture

remained clear. After more than eight hours of heating, the mixture was removed from the hot plate and cooled to room temperature. At room temperature, the mixture became very turbid and viscous.

[0052]   Emulsion polymerization of linseed and safflower acrylates and methacrylactes were prepared by Joshi (1978). The alcohol were first prepared by Rheberg's (1946) procedure involving the alcoholysis of methyl acrylate or methyl methacrylate in the presence of an acid catalyst and a polymerization inhibitor. In a one liter two-necked round-bottomed flask are placed 200 grams of soybean resin and 50 grams of methyl acrylate, 2 grams of hydroquinone, and 500 milligrams of p-toluenesulfonic acid. The flask is attached to an all-glass fractionating column without packing and the solution is heated to a temperature of $100^{\circ}C$ using a heating mantle and stirred with a magnetic stirrer. The column is operated under total reflux until the temperature of the vapors at the still head falls to $62\text{-}63^{\circ}C$ which is the boiling point of the methanol-methyl acrylate azeotrope. This azeotrope then distilled as rapidly as it is formed, the temperature at the still head not being allowed to exceed $65^{\circ}C$. When the production of methanol has become very low (6-10 hours), the excess methyl acrylate is distilled. The soybean resin methacrylate mixture is extracted with suitable solvent(s) to remove the hydroquinone and p-toluenesulfonic acid. The soybean resin methacrylate is characterized by IR spectroscopy. All polymerization reactions were carried out in emulsion using

43

the standard procedure of Fisher and Mast (1940) suitably modified to meet our requirements. The exact procedure followed is described below. A 250 ml capacity ground-glass joint Erlenmeyer flask, carrying a Teflon-enclosed magnetized stirring bar and fitted with a reflux condenser, is charged with 40 ml of deionized water, 200 mg of Triton X-100, 200 mg of SLS-Liquid, and 1-2 mg of ammonium persulfate. The solution is stirred slowly on a hot plate with magnetic stirring, and 50 grams of soybean resin methyacrylate is added into it. Heat is initially applied to induce polymerization and thereafter continued at a rate just sufficient to cause gentle refluxing. The polymerization is considered to be completed when the emulsion becomes very viscous. The viscous material is then shaken shaken with warm water and the suspension centrifuged. The process is repeated two or three times to remove the surfactant completely. The mass is then dried in a vacuum and films cast on tin plates (1 mil, dry).

[0053]   Vinyl and allyl ester of soybean resin were prepared using the method of Swern and Jordan (1948). In a 500-ml round bottom three-necked flask provided with a thermometer, a reflux condenser, and a gas inlet tube through which steam or nitrogen is passed are placed 100 grams of freshly of freshly distilled vinyl acetate and grams of 200 grams of soybean resin viscosity Z-6. and 1.6 grams of mercuric acetate is added. The mixture is shaken by hand for about 30 minutes, and 0,15 ml of 100% sulfuric acid is

44

added dropwise. The solution is heated under reflux for 3 hours, then 0.83 grams of sodium acetate trihydrate is added to neutralize the acid. The excess vinyl acetate is recovered by distillation at atmospheric pressure (vapor temperature about 70-80°C) until the solution temperature reaches 125°c. The distillation is completed at 10 mm of Hg or lower.

[0054] Polymerization is carried out in one ounce screw cap bottles equipped with oil resistant gaskets and perforated caps so that small samples could be removed with a hypodermic syringe without opening the bottles. The bottles were charged with soybean resin vinyl ester and 3% d-t-butyl peroxide. The bottles were heated by suspending them in an oil-bath maintained at the desired temperature. The polymers are isolated by stripping the monomers *in vacuo* (0.1 mm) at a maximum temperature of 200°C, and extracting the residue repeatedly with methanol.

[0055] Soybean X - Y, TAGO 310 grams, is added into a closed reactor and purged with nitrogen for a few minutes. The oligomer is heated to about 260°C with constant stirring. The stirring is continued throughout the reaction. Dicyclopentadiene, 104 ml, is added at a slow addition rate of 0.4 to 0.6 ml/min at the bottom of the vessel under the hot TAGO. After the addition of dicyclopentadiene is complete, the reaction mixture is kept at 260°C for 3.5 hours with stirring. Then the mixture is stripped at 1mm Hg for 30 minutes and removed from the reaction vessel. The product is cooled to room temperature.

[0056] Soybean oligomer Z - 6(TAGO), 500 grams, is heated to 145°C and 1000g of myrcene and 10 grams of di-*tert*-bu peroxide is added. The reaction is continued for 6 hours at 140-150°C. The modified TAGO is treated with .05% Co and heated in a dryer.

[0057] Vegetables oils as an alternative diesel and fossil fuel is limited by their high viscosity. Several routes have been tried for reducing this viscosity and most recently has been the direct catalytic upgrading of the vegetable oils to produce liquid fuels. The catalytic cracking of vegetable oils, which is nothing more than reduction of the molecular weight and viscosity, gives several types of products, either gaseous, solid, or liquid. Numerous reports are given in the literature for the catalytic cracking of soybean oil and other vegetable oils. Most investigations have shown that the products obtained from the cracking process are comparable to diesel fuel but not to fossil fuel. The physical properties and chemical compositions of bio and fossil fuels were determined by Pioch (1993). The results showed that the aromatic content of fossil fuel is higher than the aromatic content of biofuels. The olefin content is in the same range as well as the saturated branched chain hydrocarbons. The octane number for fossil fuel was reported as 90 and that of catalytically cracked copra and palm stearine were 91 and 86 respectively. Concerning the diesel fractions, the chemical compositions are close to the fossil fuels The biodiesel fuel had a high content of normal paraffin, no olefins and no heavy

46

hydrocarbons and similar aromatic content as the fossil diesel fuel. Kobayashi (1921) distilled soybean and coconut oil mixed with kaolin at approximately 700° C decomposed to give " vegetable petroleum" or biofuel. During world war II, Chang (1947) reported that large scale decomposition of tung oil and soybean oil was carried out in large scale batch reactors in China, with the use of acid($AlCl_3$) or basic (MgO, CaO, NaOH) catalysts.

[0058]   Attempts to produce fuel that could be gasoline substitute, i.e. contain a significant fraction of aromatics are reported in the literature. Novella (1984) applying ZSM-5 type zeolites in acid form transformed various kinds of vegetable oils to hydrocarbon fuel. The use of soybean oligomer as a feed stock for catalytic cracking to increase the aromatic content of biofuels is evident from the proposed chemical structure of the repeating unit. As described in the introduction the Diels-Alder diene synthesis has received the most support from data collected for the polymerization mechanism of TAGS. This mechanism, wherein a diene and a dienophile combine to form a cyclohexene structure is supported by data showing the presence of cyclic structures in polymerized oils. It is therefore proposed to investigate the formation of biofuels with high aromatic content by reductive catalytic hydrocracking of TAGOS of differing viscosity. Filho (1993) reported a production yield (weight % of feed) using soybean oil of 66.6% alkanes, 11.9% cycloalkanes, 4.3% alkylbenzenes. The authors concluded that depending upon

47

the multifunctionality of the catalyst, isomerization, cyclization, and aromatization processes can occur during hydrocarbon fuel production from vegetable oils. Using a similar approach with the resin, it is the expectation to obtain a biofuel that is high in aromatic content comparable to fossil fuel due to existence gcyclic structures in TAGOS.

[0059]   Reductive catalytic hydrocracking will be with either a two gallon or a $50cm^3$ (Autoclave Engineering) stainless steel batch reactor equipped with a stirrer, and the temperature and pressure limits being $450^{\circ}C$ and 25MPa respectively. The feedstock consists of soybean resin with viscosity of 500 poises and 1000 poises using catalysts precursors of NiMo/ - Al_2O_3 and Ni/SiO_2 (2 wt % based on resin) and elemental sulfur (1.7 5 wt % based on resin). The procedure of Filho (1993) was followed.

[0060]   Maplewood shavings, 16.1 grams, and soybean oligomer Z- 6, 53.5 grams, were mixed together until all shavings of maplewood were covered with the oligomer. The mixture was placed in a 8-1/2 cm daimeter x 7mm thick brass dish. Hot air was blown over the mixture for one hour. The mixture was placed in a convection oven at $75^{\circ}C$ for 26 hours. The board was removed and allowed to cool to room temperature and examined. The board was spongy.

[0061]   Addition of sodium hydroxide to soybean Z-6 on standing formed a solid polymer film.

[0062]   Addition of sodium hydroxide to soybean X - Y on standing formed

a turbid solution and a lot of foam when shaken.

[0063]   Lawn grass with long stems and long blade-like leaves was cut into small pieces and dried.   The grass sample was then placed into a mill and reduced to small fragments.   A small mesh screen was used to separate the smallest pieces from the larger pieces.   The smaller pieces were used for the preparation.   Grass, 2.0 grams, was mixed with SBO, 200 grams, in an Erlenmeyer flask.   The mixture was stirred and placed on a hot plate.   After approximately one hour of heating the mixture turned a very dark green.   The mixture was heated for a total of twenty one hours, removed from the hot plate and allowed to cool to room temperature.   The viscosity of the mixture was determined.

Table 44. Viscosity Data for Complex Between Triacylglycerol Oligomers and Gramineae (Grass)

TAGOS	TAGO VISCOSITY	COMPLEX VISCOSITY
SOYBEAN	22,683cp	33,367cp
COTTONSEED		
SUNFLOWERSEED		
CORN		

[0064] Johnson's pure cotton balls, made from 100% pure, non-chlorine bleached cotton, was purchased from a local drug store. One cotton, which weighed 0.3 grams, was pulled into small pieces and added one at a time to an Erlenmeyer flask containing 203 grams of SB(Z-6) which had been heated to 100°C. The mixture was stirred and placed on a hot plate. After heating for approximately seven hours at 110°C the cotton started to form gelatinous mass. It was not observable whether the liquid portion of the mixture was also becoming more gelatinous. Continued heating of the mixture resulted in the cotton becoming almost completely gelatinous. The mixture was removed from the hot plate after 40 hours of heating. The viscosity of the liquid portion was measured.

Table 45. Data for Complex Between Triacylglycerol Oligomers and Cotton

TRIACYLGLYCEROL OLIGOMER	COMPLEX VISCOSITY, P
SOYBEAN (Z-6)	>8,000,000cp
COTTONSEED	
SUNFLOWERSEED	
CORN	

[0065] Removal of ink from paper substrate is done commercially using ink removal solutions containing hazardous materials. It has been previously shown that TAGOS can be emulsified using water and a surfactant. Paper

printed with TAGOS inks are easily dissolved in a solvent system using non-hazardous water-based cleaning solutions which emulsifies the ink and can be reused several times before it has to be replaced. The ink solution is filtered to remove the deinked paper slurry which can then be further processed to produce recycled paper.

Table 28. Formulation of Ink Removal Solution #1

CONSTITUENT	PERCENT
PART A*	89.07
WATER	85.07
SWS	0.1122
DYE	1.68
MONOETHA NOLAMINE	2.25
NA4EDTA	2.81
DIPROPYLENEGL; YCOLMETHYLETHER	3.37
WITCONATE 90 K	4.27
PART B*	10.93
TRITON X-100	64.04
HYAMINE	8.51
SCENT	27.45

Table 29. Formulation of Ink Removal Solution #2

CONSTIUENT	PERCENT
TRITON X-100	1
POTASSIUM HYDROXIDE (37.4%)	13.37
WATER	85.63

[0066]   Approximately three drops of red ink was placed on a 5" x 8" piece of white papter and drawn down with a putty knife making an ink strip approximately 3" in width. A length of approximately 2" was cut and used for the test.

[0067]   In one Erlenmeyer flask was placed 100 ml of formula #1 cleaning solution along with the test specimen. In another Erlenmeyer flask was placed 100 ml of formula #2 cleaning solution along with the test specimen. Both solution were shaken and allowed to stand. Periodically on several occasions they were shaken again. Ink began to be removed immediately with formulation #1 as evidence by the solution forming a reddish color. With formulation #2 color was being removed as evidence by the fading of the test specimen.

[0068]   The mixture obtained from printed paper is filtered and the solution decanted. The paper slurry remaining is mixed with and emulsion prepared using soybean oligomer Z - 6(25%), triton X-100(5%), and water (70%). The mixture is filtered and then dried by passing through pads heated to 75°C. A

sheet of recycled paper is formed.

[0069] TAGOS interaction with metals and water were examined. The examination was to determine differences in the interaction between metal-TAGO complex and water-TAGO complex. Soybean oligomer Z - 6 and X - Y, 5 grams each, were placed in separate containers of 95 grams of distilled water. The mixtures were stirred and allowed to stand at room temperature. The same procedure was repeated with 0.2m potassium hydroxide solution.

[0070] Both soybean oligomers X - Y and Z - 6 had formed two layers. The aqeuous layer was slightly turbid and a white oily layer. Upon standing at room temperature for a long period of time, soybean oligomer Z - 6 formed a rubbery, spongy mass. This mass is probably due to the interaction of air, water and the oligomer.

[0071] Water was added to a beaker which contained soybean oligomer crosslinked with BLG. The mixture was heated to boiling. The sides of the beaker were scraped with a spatula. Upon cooling, polymer particles were floating in the water. The particles were removed from the water and allowed to dry. Upon drying, the small particles formed clear plastic pieces. The plastic pieces were very elastic and stretched when pulled. The plastic pieces were soft and spongy.

[0072] Upon addition of 0.2m KOH to soybean oligmer X - Y, the solution turned milky white with no formation of oil droplets. A foamy layer was on top.

Upon addition of 0.2 m KOH to soybean oligmer X - 6 it also formed a milky/cloudy solution with a foamy layer on top. However, upon standing for a long period of time, soybean oligomer X - Y produces large amount of foam when shaken with no visible large particles present. The solution, however, is still turbid. In the case of soybean oligomer Z - 6, the mixture does not produce a lot of foam when shaken, and it contained solid particles.

[0073]   Thus, in accordance with the present invention, there has been provided triacylglycerol oligomers and methods for making and using same that fully satisfies the objectives and advantages set forth above. Although the invention has been described in conjunction with the specific drawings and language set forth above, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the invention.